



Decontamination of Chemical Agent Simulant by Nanometal Oxides

**by Nicole E. Zander, Eileen Kowalski,
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14. ABSTRACT The ability of a U.S. Army vehicle or a piece of equipment to decontaminate itself in situ from the threat of chemical agents is highly desirable and may reduce the weight and logistical footprints associated with decontamination operations. This work explores the ability of several nanometal oxide powders (that could potentially be incorporated into U.S. Army coatings) to decontaminate 2-chloroethyl ethyl sulfide, a simulant for the blister agent sulfur mustard. Another mustard stimulant, 2-chloroethyl phenyl sulfide, and a simulant for the nerve agent GB, dimethyl methylphosphonate, were also examined.					
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1. Background

U.S. Army vehicles and support equipment currently employ highly cross-linked chemical agent resistant coatings to repel chemical hazards. Likewise, materials used in individual soldier protective clothing are designed to repel and/or absorb agents in order to protect from these threats. Many chemical warfare agents are highly persistent, especially in their polymer thickened form, and the threat to soldiers remains until the vehicle, equipment, or clothing can reach a safe zone to be decontaminated by conventional methods. The ability for a material to decontaminate itself in situ is therefore highly desirable and may reduce the weight and logistical footprints associated with decontamination operations. To maintain the critical performance characteristics of the coating or fabric, a minimal amount of active material is preferred to reduce the overall impact on bulk physical properties.

Nanometal oxide coatings have been shown to decontaminate chemical agents and their simulants (1–7). These findings often result from protocols that do not reflect conditions likely to be encountered in the field. This work explores the ability of several nanometal oxide powders to decontaminate 2-chloroethyl ethyl sulfide (CEES), a simulant for the blister agent sulfur mustard (HD). Another mustard stimulant, 2-chloroethyl phenyl sulfide (CEPS), and a simulant for the nerve agent GB, dimethyl methylphosphonate (DMMP), were also examined.

2. Experimental Procedure

2.1 Materials and Instrumentation

NanoActive^{*} Aluminum Oxide Plus, Copper Oxide, Magnesium Oxide Plus, Cerium Oxide, Titanium Oxide, Zinc Oxide, and FAST-ACT were purchased from NanoScale Materials, Inc. Triton Systems, Inc. (TSI) provided a series of magnesium oxide samples that had been heated at different conditions (described in table 1). TSI also supplied a titanium oxide sample and coated aluminum and magnesium oxides. Two different titanium (IV) oxides (anatase) were obtained from Aldrich and Alfa Aesar, and an aluminum oxide was obtained from Aldrich. All simulants were purchased from Aldrich. The two major breakdown products for CEES, ethyl vinyl sulfide and ethyl 2-hydroxy ethyl sulfide, were obtained from Aldrich and Acros, respectively.

^{*}NanoActive is a trademark of NanoScale Materials, Inc.

All NanoActive materials were prepared by the company using an aerogel procedure to generate a mesoporous spongelike network of interconnected nanoparticles. Most of these particles contain greater than 50% porosity by volume and achieve extremely high surface area due to the increased area produced by the pores (8). TSI samples were prepared using a sol gel procedure and baked at the indicated temperatures in table 1. The metal oxides purchased from Aldrich and Alfa Aesar have lower respective surface areas, as the surface areas were not enhanced through one of the former procedures. Table 1 shows a summary of all metal oxides exposed to CEES extracted in isopropyl alcohol. Calculations for the composition of products are based on relative peak areas. Recovery determinations are based on starting amount of CEES and calculated amounts of CEES and other products based on a five-point linear calibration vs. the amount of CEES recovered in the controls using averaged values. The far right column portrays the absolute amount of CEES after 24 hr based on the amount recovered from the controls (based on average area counts).

Table 1. Summary of results for all metal oxides exposed to CEES extracted in isopropyl alcohol.

Metal Oxide	CEES (%)	Elimination Product (%)	Hydrolysis (%)	Recovery Products vs. Control (%)
NanoActive Al ₂ O ₃	20.0 ± 3.7	7.7 ± 2.1	69.0 ± 1.9	74.9 ± 4.9
NanoActive MgO	47.4 ± 0.2	3.6 ± 0.1	46.6 ± 0.2	97.9 ± 10.1
NanoActive ZnO	88.8 ± 1.4	2.1 ± 0.3	8.5 ± 1.5	120.3 ± 28.4
NanoActive CeO ₂	94.9 ± 0.7	1.1 ± 0.0	1.9 ± 0.3	107.9 ± 1.8
NanoActive CuO	90.5 ± 1.0	2.0 ± 0.1	6.0 ± 0.9	118.8 ± 0.5
NanoActive TiO ₂	75.1 ± 1.9	0.0 ± 0.0	24.9 ± 1.9	94.7 ± 4.6
Fast Act	77.1 ± 3.8	7.3 ± 0.0	13.6 ± 3.5	96.3 ± 7.9
NR3-121 (MgO 80 °C, 12 hr)	97.0 ± 0.3	1.9 ± 0.1	1.1 ± 0.1	132.9 ± 1.3
NR3-122 (MgO 250 °C, 24 hr)	98.7 ± 0.1	1.3 ± 0.1	0.0 ± 0.0	152.2 ± 20.5
NR3-123 (MgO 350 °C, 24 hr)	94.5 ± 1.1	5.2 ± 0.9	0.0 ± 0.0	143.0 ± 18.2
NR3-124 (MgO 450 °C, 24 hr)	94.3 ± 1.2	4.7 ± 1.0	0.8 ± 0.1	118.9 ± 7.4
NR3-125 (MgO 500 °C, 24 hr)	95.0 ± 0.8	3.7 ± 0.6	1.1 ± 0.2	140.9 ± 25.6
NR3-126 (MgO 550 °C, 24 hr)	94.9 ± 0.5	3.8 ± 0.1	1.1 ± 0.4	149.3 ± 15.9
NR3-127 (MgO, 700 °C, 24 hr)	97.7 ± 0.2	1.5 ± 0.1	0.8 ± 0.1	119.6 ± 9.9
NR3-128 (TiO ₂ , 80 °C, 24 hr)	93.2 ± 0.7	1.3 ± 0.2	5.4 ± 0.8	117.4 ± 22.2
LCK-4-054 A (coated Al ₂ O ₃)	91.3 ± 2.0	1.6 ± 0.1	6.1 ± 1.7	117.6 ± 2.7
LCK-4-054 B (coated MgO)	98.1 ± 0.0	1.2 ± 0.0	0.7 ± 0.0	123.7 ± 15.8
Bulk Al ₂ O ₃	85.2 ± 1.4	2.8 ± 0.0	11.4 ± 1.1	142.9 ± 31.5
Bulk TiO ₂ Alfa Aesar	99.1 ± 0.0	0.0 ± 0.0	0.9 ± 0.0	123.0 ± 13.8
Bulk TiO ₂ Aldrich	82.1 ± 1.7	0.6 ± 0.2	16.9 ± 1.9	137.3 ± 10.2

Samples were analyzed using a HP5890 series II gas chromatograph with a HP5972 mass selective detector. The injector and detector temperatures were 250 and 280 °C, respectively. The column was a Phenomenex ZB-50 (30-m × 0.25-mm inner diameter × 0.25-μm film thickness). The column was maintained at 40 °C for 3 min, and then increased to 250 °C at 10 °C/min. The solvent delay was 3 min. The instrument was calibrated prior to each analysis with a five level curve of the simulant (and breakdown products for the CEES calibration) with

concentrations ranging from 0.1 mg/mL to 3 mg/mL. The low level standards were analyzed at the end of each sequence to verify instrument sensitivity.

2.2 Reaction of HD and GB Simulants With Metal Oxide Powder

Approximately 20 mg of a simulant was added to 100 mg of metal oxide powder (weight fraction metal oxide powder = 0.83) in a 20-mL glass I-Chem^{*} vial. All samples were vortexed for 30 s to promote contact between the simulant and the powder. Samples were then set at room temperature for 24 hr. No efforts were made to control ambient light or humidity. Aliquots of the simulant in an empty vial served as controls. All samples and controls were prepared and analyzed in duplicate.

2.3 Extraction of CEES and Its Decontamination Products

After 24 hr, 3 mL of extraction solvent (usually isopropyl alcohol) was added. Other solvents evaluated were acetone, acetonitrile, methylene chloride, and pentane. After adding the extraction solvent, 15 μ L of toluene was added to each vial to serve as the internal standard. Samples were shaken for 2 hr on a wrist-action shaker. All samples were filtered through Acrodisc 0.45- μ m PTFE syringe filters prior to gas chromatography-mass spectrometry (GC-MS) analysis.

3. Results and Discussion

3.1 Effectiveness of Metal Oxides in Decontaminating CEES

Various metal oxide powders were reacted with CEES. Only the NanoActive Aluminum Oxide Plus showed appreciable decontamination of CEES after 24 hr. The same metal oxides from other manufacturers did not produce similar levels of decontamination, perhaps because of the preparation of these materials. However, even the highest decontamination observed (~80%) was below what would be needed to effectively decontaminate a vehicle exposed to a chemical agent in the field. Results for all metal oxides tested are summarized in table 1. The NR3 and LCK powders were from TSI.

Typical decontamination routes were elimination of the chlorine to yield $\text{CH}_2=\text{CH-S-CH}_2\text{CH}_3$ (retention time, 4.1 min) or hydrolysis to produce $\text{HOCH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_3$ (retention time, 10.2 min) (3). A late-eluting peak at 14.5 min (enchained product) was also seen, consistent with previous results from this lab. The proposed structure for this compound, $\text{Cl-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_3$, is consistent with mass spectra. Synthesizing this compound to establish its retention time would be required to verify this structure, but it is unnecessary because the latter

^{*}I-Chem is a registered trademark of Nalge Nunc International.

comprises an insignificant portion of the product distribution. Figure 1 displays a typical chromatogram of a cocktail extract from exposure of NanoActive magnesium oxide. Peak a is the elimination product, $\text{CH}_2=\text{CH-S-CH}_2\text{CH}_3$. Peak b is the internal standard, toluene. Peak c is CEES. Peak d is the hydrolysis product, $\text{HOCH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_3$. Peak e is the enchainment product, $\text{Cl-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_3$.

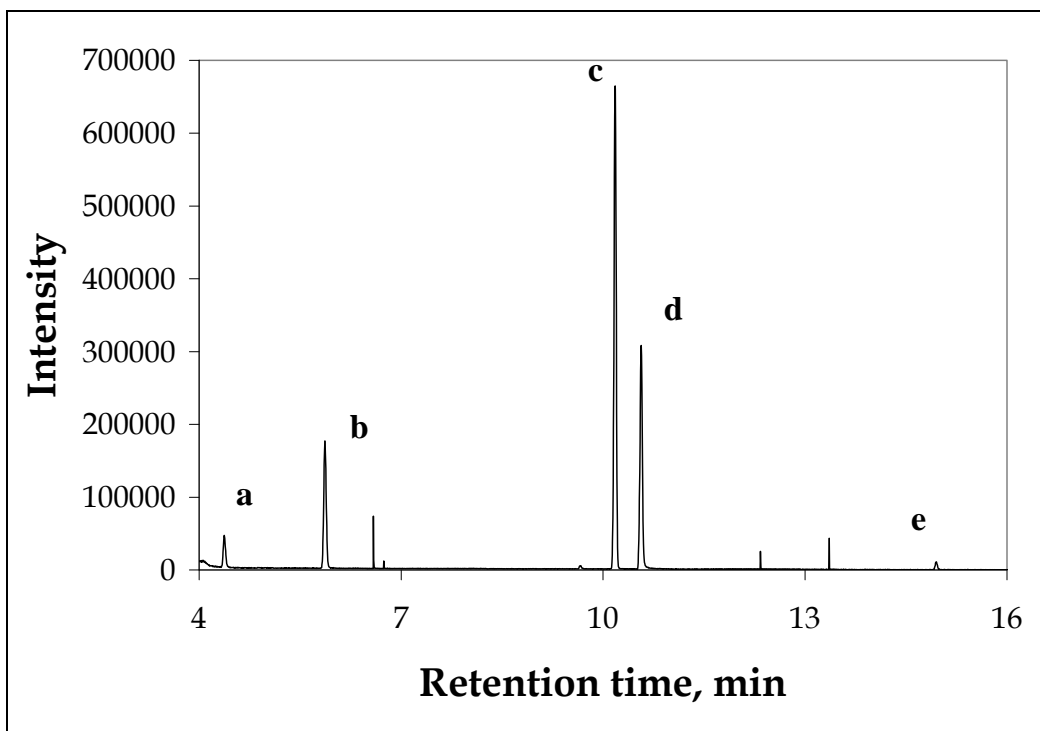


Figure 1. Chromatogram of cocktail extract from exposure of NanoActive Magnesium Oxide Plus to CEES for 24 hr.

3.2 Effectiveness of Metal Oxides in Decontaminating CEPS and DMMP

DMMP and CEPS were tested with NanoActive Aluminum Plus, Magnesium Plus and Cerium Oxides to determine their efficacy against other simulants. The mechanism for the decomposition of DMMP initiates with the cleavage of the phosphorous methoxy bonds, followed by protonation to form methanol. A secondary product (dimethyl ether) is formed by an acid catalyzed dehydration of methanol (9). No breakdown products of DMMP were observed during GC-MS analysis, which may be due to a slow reaction that occurs with the metal oxide or to the volatility of the reactant, which caused the DMMP to reside in the headspace of the vial rather than diffusing through the metal oxide. For the latter reason, DMMP breakdown studies are usually performed with the gaseous form passing through an adsorbent bed at a set flow rate and stream composition, and breakthrough is calculated. In a study by Mitchell et al., 25 mg of DMMP was decomposed per gram of metal oxide (9).

CEPS decomposes with a similar mechanism as CEES—the chlorine is displaced to form the elimination product. This product then undergoes hydrolysis to form the major product. GC-MS analysis revealed both breakdown products, but in much smaller amounts when compared to the CEES reaction with the identical metal oxide and conditions. In the best replicate, only 30% of the recovered product was decontaminated, whereas CEES on NanoActive Al_2O_3 achieved 80% relative decontamination. Possibly, the phenyl group inhibits the formation of the cyclic intermediate sulfonium ion, which readily forms in CEES and HD, allowing rapid hydrolysis. The reaction on the metal oxides is mostly diffusion limited, so CEES, with its lower boiling point/higher vapor pressure and, hence, greater diffusion rate, is able to diffuse and react faster (7).

3.3 Desorption of CEES and Its Products

Recovery of CEES and its decontamination products sometimes varied widely between metal oxides (see table 1). Some of this variability may be from adding the CEES directly to the solid metal oxide powder. Although samples were vortexed to mix the CEES and metal oxides, it is unlikely that the two reactants were uniformly mixed.

Researchers from Kansas State University determined that a solvent facilitated contact between the reactants, as the diffusion of CEES is a major limiting factor in decontamination. The solvent/metal oxide slurry procedure was attempted with pentane, the solvent utilized in Martin et al. (5), but extractions of the products were inadequate. In fact, only 1% of the reactant CEES was recovered, and no breakdown products were observed. Either the metal oxide adsorbed the CEES and the solvent was unable to extract it, or most of the CEES was converted to products not soluble in the extraction solvent. The same method was attempted a second time with a more polar solvent (isopropyl alcohol) and 80% of the CEES was recovered with no breakdown products detected. In the latter experiment, the isopropyl alcohol might have prevented the CEES from reacting with the metal oxide because of solubility effects.

3.4 Extraction Solvent Efficacy

Various extraction solvents were tested using the dry method mentioned in the procedural section. The solvents examined were pentane, methylene chloride, acetone, isopropyl alcohol, and acetonitrile. The efficacy of the extraction solvents was determined by the recovery of the sum of CEES and its breakdown products. The order of solvent extraction efficiency was found to be: isopropyl alcohol > acetone = acetonitrile > methylene chloride > pentane.

3.5 Surface Area, Density, and Wetness of Metal Oxide

Table 2 displays the results from an experiment in which the weight-percent of the NanoActive Al_2O_3 varied and the effect of drying the powder overnight at 100 °C. Clearly, the amount of aluminum oxide affects the decontamination ability, because the surface area available for interaction changes. The percent recovery of products also appears influenced by the amount of powder present; higher recoveries are obtained when less powder is used. The many powders

Table 2. Summary of varying the weight-percent and drying of NanoActive Al₂O₃.

Metal Oxide (mg)	CEES (%)	Elimination Product (%)	Hydrolysis (%)	Recovery Products vs. Control (%)	CEES vs. Control (absolute) (%)
Al ₂ O ₃ , as received—100	25.3 ± 2.6	5.9 ± 0.4	67.8 ± 2.3	74.9 ± 4.9	11.5 ± 1.2
Al ₂ O ₃ , as received—200	9.5 ± 1.4	5.6 ± 0.6	84.5 ± 0.9	87.5 ± 12.1	5.2 ± 1.8
Al ₂ O ₃ , as received—50	61.8 ± 7.1	5.6 ± 0.3	31.4 ± 7.2	96.3 ± 12.0	40.9 ± 0.8
Al ₂ O ₃ , dried—100	39.3 ± 2.5	6.2 ± 0.5	54.1 ± 2.2	58.7 ± 8.5	23.6 ± 4.9

tested with identical weight-percents gave drastically different volumes of powder, thus varying total surface areas. NanoActive Aluminum Oxide, as received, was the least dense of all the powders and was undoubtedly the most effective at breaking down CEES. In addition, the wetness of the powder also affected the decontamination ability of the metal oxide—hydrolysis was the major breakdown mechanism. Because of reduced moisture, the dried aluminum oxide was less effective than the as-received product. The relative percentage of elimination product was not affected; only the hydrolysis product was reduced in the dried form. Their inefficacy is partially explained by the fact that all the TSI metal oxides were also dried.

A linear correlation can be drawn between the surface area of the metal oxide nanoparticle and the efficacy of CEES decontamination. Table 3 displays several physical characteristics (including surface area, density, and particle size) of the various metal oxides examined. Physical characteristics were obtained from manufacturer product data sheets. True densities may vary from pure densities of the metal oxides as some samples may contain silica. Figure 2 displays the former relationship and demonstrates that the surface area appears to be more important than the type of metal oxide in the decomposition of CEES, with the exception of NanoActive Titanium Oxide. Figure 3 displays the relationship between the volume of the metal oxide and decontamination. The lower-density metal oxides are more efficient in converting CEES to breakdown products on a constant weight fraction basis as a larger volume of nanoparticles (and, thus, more active sites for reactions to occur) is available. There appears to be a weak correlation between moisture content and decontamination, which increases with increasing wetness and is expected as the major breakdown mechanism is hydrolysis. The results in table 2 confirm this trend. More experiments would be needed to determine optimal moisture levels. Although density, surface area, and moisture content were influential in decontamination efficacy, particle size did not appear to be a determining factor.

Table 3. Physical characteristics of various metal oxides.

Metal Oxide	Surface Area (m ² /g) (BET)	Mean Aggregate Size (μm) (d _{0.5})	Pore Diameter (Å)	True Density (g/cm ³)	Moisture Content (%)
NanoActive Al ₂ O ₃ Plus	550	5	100	2.9	12
NanoActive MgO Plus	600	12	30	2.4	3
NanoActive ZnO	70	4	170	5.6	2
NanoActive CeO ₂	50	9.5	70	6.0	3
NanoActive CuO	65	6	85	5.7	4
NanoActive TiO ₂	500	5	32	3.7	4
Al ₂ O ₃ (Aldrich)	155	—	—	—	—
TiO ₂ (Alfa Aesar)	45	—	—	3.9	—
TiO ₂ (Aldrich)	220	—	—	3.9	—

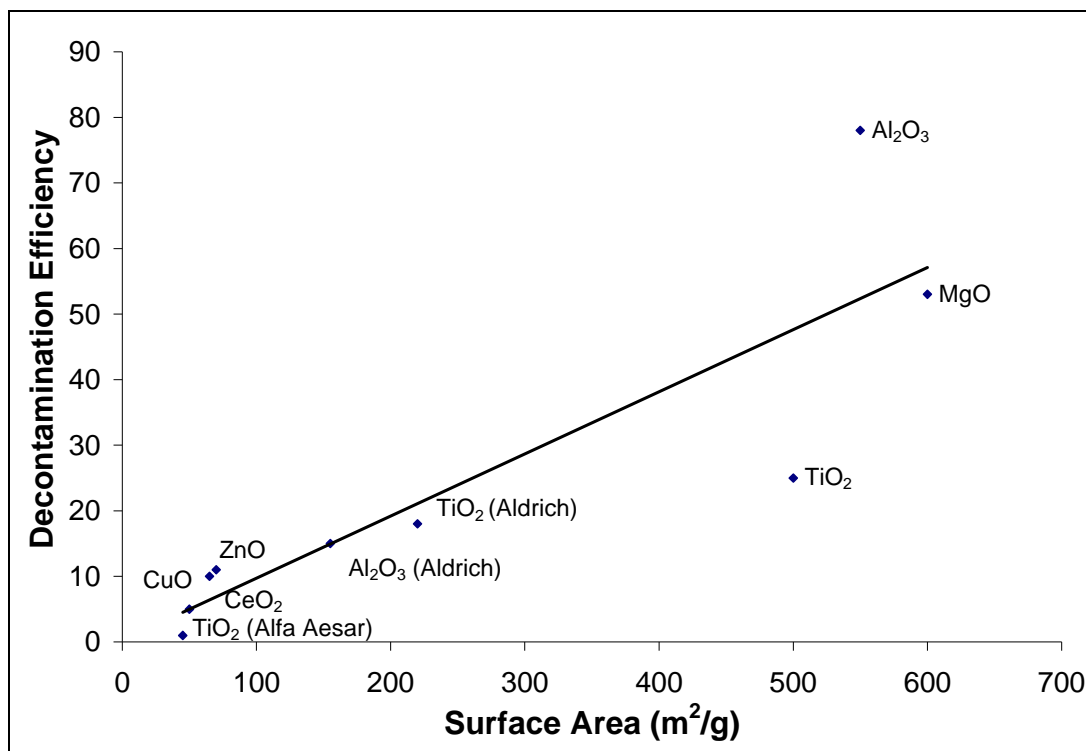


Figure 2. Correlation between the surface area of the metal oxide and decontamination of CEES.

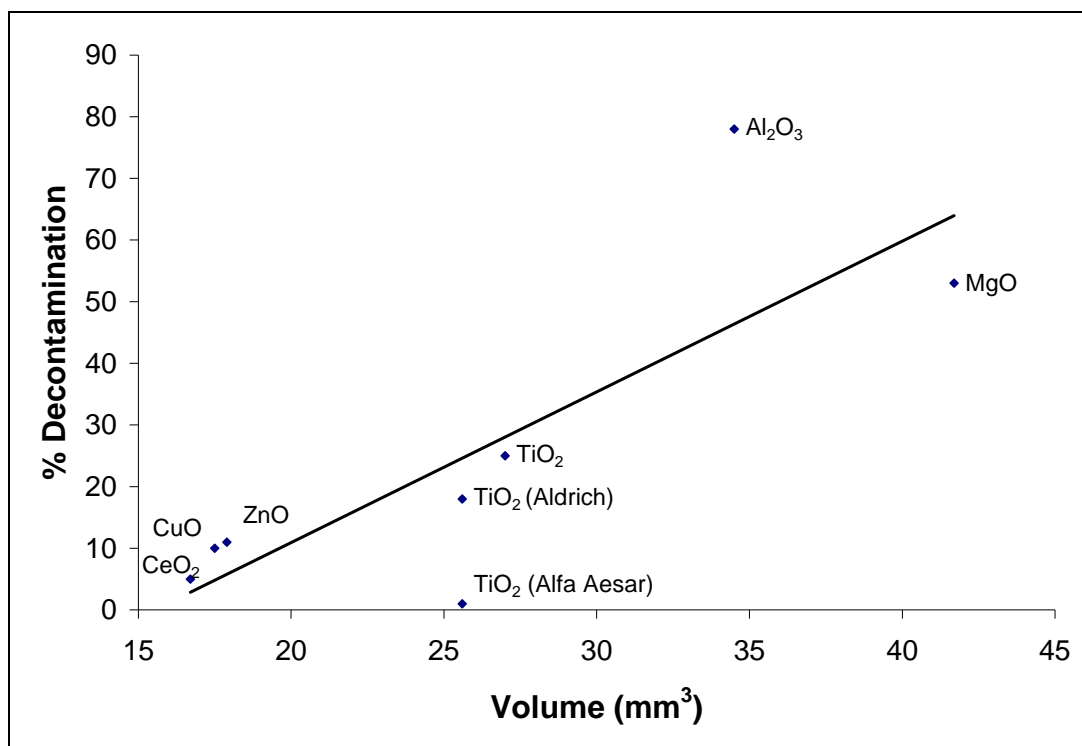


Figure 3. Correlation between the volume of the metal oxide and decontamination of CEES at a constant weight fraction of metal oxide equal to 0.83.

4. Conclusions

Metal oxides have the potential to mitigate some of the deleterious effects of chemical agents. A survey of various metal oxides demonstrated that the high surface area Al₂O₃ was superior to the other metal oxides in the decontamination ability. Since MgO is an alkaline metal, it was expected to more easily facilitate the nucleophilic displacement and H-Cl elimination reactions than Al₂O₃ (5). Therefore, inherent surface reactivity does not completely account for the observed results. The surface area of the nanoparticle is extremely important in determining a product's efficacy in decontamination—higher surface areas allow more active reaction sites. The ratio of volume of material to simulant varied widely between the different metal oxides examined because of density variations. The lighter materials provided a larger overall volume with which to encompass the simulant. In addition, the wetness of the metal oxide appeared to contribute to the material's overall effectiveness. At least for the NanoActive Al₂O₃, the as-received material was 80% more effective than the same material dried overnight at 100 °C.

Several researchers claim to have achieved full decontamination of the CEES stimulant in less than 4 hr, as opposed to achieving approximately 80% decontamination in 24 hr (5). Many of the former experiments were performed with 5 weight-percent CEES, whereas the latter experiments

utilized 20 weight-percent CEES. A minimal amount of material was utilized in the experiments—the metal oxides were intended to be put into coatings without altering their properties. The results in table 2 demonstrate that more material increased the decontamination ability; hence, it is likely that a sufficiently low weight-percent of CEES would have allowed full decontamination.

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